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On the Dielectric Relaxation in Ferrites due to Electron Hopping at Low Temperatures

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Dielectric dispersions were found in the powder samples of Fe_3O_4 , $\text{Mn}_{1.4}\text{Fe}_{1.6}\text{O}_4$, $\text{Mn}_{0.8}\text{Fe}_{2.2}\text{O}_4$, $\text{Zn}_{0.6}\text{Fe}_{2.4}\text{O}_4$ and $\text{Mn}_{0.59}\text{Zn}_{0.33}\text{Fe}_{2.08}\text{O}_4$ at temperatures from 77 to 4.2 K. The dielectric relaxations were connected with the existence of Fe^{2+} ions and the magnitudes of dielectric dispersion were roughly proportional to the amounts of Fe^{2+} ions in the samples. The activation energies obtained from the temperature dependences of electrical conductivity were close to those obtained from dielectric relaxation. The dielectric relaxation was considered to be caused by the hopping of electron between Fe^{2+} and Fe^{3+} ions on the octahedral sites in the spinel structure.

INTRODUCTION

Transition metal oxides such as Fe_3O_4 and various ferrites contain some different valent metal ions in a sample. In Fe_3O_4 and ferrites Fe^{2+} and Fe^{3+} ions exist at the same time in the sample. It is well known that the hopping of electron between Fe^{2+} and Fe^{3+} ions reduces the electrical resistivity of the oxides. In Fe_3O_4 above 119 K (the Verwey transition temperature) Fe^{2+} ions interchange electrons with Fe^{3+} ions, and the electrical resistivity becomes low, but below the transition temperature Fe^{2+} ions occupy the fixed cation site in the crystal. The crystal structure transforms from cubic to orthorhombic through the transition temperature. This transition is called the Verwey order-disorder transition. There are some recent reports^{1,2)} on the crystal structure of low temperature phase which insist on the existence of crystal structure with different unit cells.

In the previous work³⁾ we found the heterogeneous structure in particles of Fe_3O_4 and some ferrites, namely the oxidation of the surface layers is much higher than that of inner parts in powder samples (about 1 μ diameter). The resistivity of oxygen rich phase is much higher than that of oxygen poor phase (ferrous ion rich phase). Therefore, interfacial polarization between these phases occurs. The dielectric relaxation arising from the interfacial polarization was observed in the temperature range from room temperature to liquid nitrogen temperature. In this work dielectric measurements were made in the temperature range from 77 to 4.2 K by using liquid helium in order to examine the dielectric properties of ferrites at low temperatures below liquid nitrogen temperature. The hopping of electron between Fe^{2+} and Fe^{3+} ions in Fe_3O_4 does not occur below 119 K. In oxidized Fe_3O_4 and ferrites the transition

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temperature shifts from 119 K (transition temperature of Fe_3O_4 ⁴⁾). At the temperature below the transition point it is considered that Fe^{2+} and Fe^{3+} ions hop along the direction of the applied a.c. electric field. Therefore, dielectric relaxation due to the hopping of electron between Fe^{2+} and Fe^{3+} ions can be expected at such low temperatures.

EXPERIMENTAL

Fe_3O_4 , $\text{Zn}_{0.6}\text{Fe}_{2.4}\text{O}_4$, $\text{Mn}_{1.4}\text{Fe}_{1.6}\text{O}_4$, $\text{Mn}_{0.59}\text{Zn}_{0.33}\text{Fe}_{2.08}\text{O}_4$, and ZnFe_2O_4 are the same samples as used in the previous paper.³⁾ $\text{Mn}_{0.8}\text{Fe}_{2.2}\text{O}_4$ was prepared from aqueous solution by the same method that was used in the preparation of the above samples.

The cryostat made of glass shown in Fig. 1 was used to measure the dielectric dispersion in the temperature range from 77 to 4 K. At first to remove water present in the powder sample, the space containing a dielectric cell was evacuated for several hours. Then it was filled with dry helium gas of 1 atm. The temperature of the powder sample was measured by an AuCo-Cu thermocouple at temperatures above 20 K and a Ge resistor at temperature below 20 K. Temperature dependence of dielectric constant and loss were measured at the frequencies of 0.1, 1, 10, and 100 KHz. We measured the frequency dependence of dielectric constant near 30 K in all ferrites. Some definite temperatures above 10 K were obtained by controlling the rate of evaporation of liquid helium in the apparatus shown in Fig. 2. The temperatures

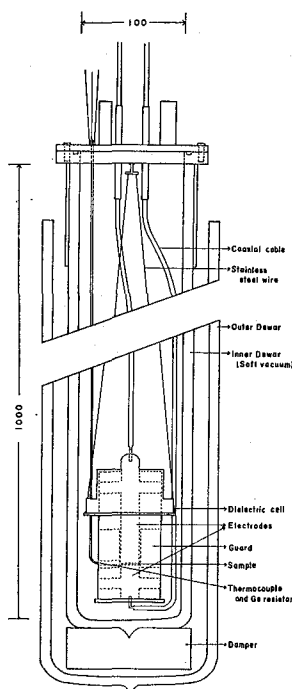


Fig. 1. Structure of the glass cryostat.

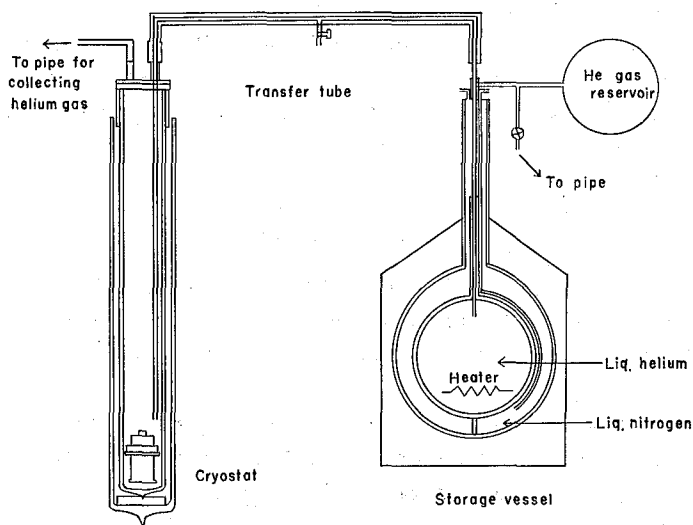


Fig. 2. Apparatus for cooling samples.

below 10 K was obtained by controlling the rate of pouring of liquid helium.

Dielectric constant and dielectric loss were measured by the use of a transformer bridge. The measurements were carried out over the frequency range of 20 Hz to 1 MHz by using the selective amplifier.

RESULTS

The temperature dependences of dielectric constant and loss of Fe_3O_4 are shown in Fig. 3, in which a relaxation is seen near 30 K. Since the conductivity of Fe_3O_4 was high, dielectric loss showed no maximum without subtracting the d.c. conductivity especially at low frequency (100 Hz). Figure 4 shows the dielectric dispersion of

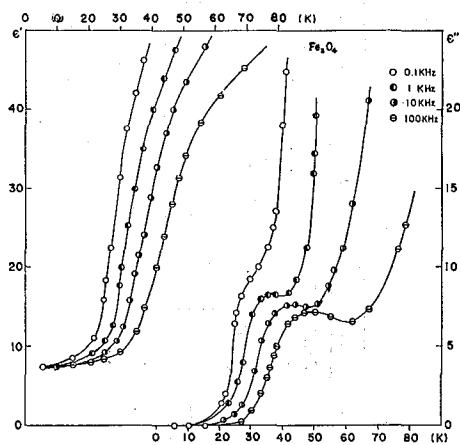


Fig. 3. Temperature dependences of dielectric constant and dielectric loss of Fe_3O_4 .

Fe_3O_4 at 37 K, whose complex plane plots (Fig. 4(b)) indicated the broad distribution of relaxation times. The curve of ϵ'' was obtained by subtracting the conductivity at 20 Hz from that at each frequency. Figure 5 shows the temperature dependence of dielectric constant and loss of $\text{Mn}_{1.4}\text{Fe}_{1.6}\text{O}_4$. Being not so highly conductive, this sample showed a clear peak of loss without subtracting d.c. conductivity. Figure 6 shows the dielectric dispersion of $\text{Mn}_{1.4}\text{Fe}_{1.6}\text{O}_4$ at 36 K. Figures 7 and 8 show the temperature dependence of dielectric constant and loss of $\text{Zn}_{0.6}\text{Fe}_{2.4}\text{O}_4$ respectively.

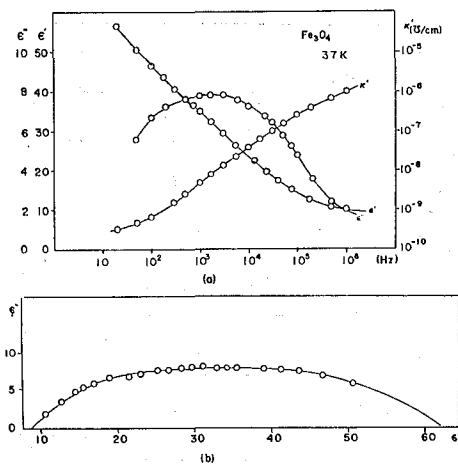


Fig. 4. (a) Frequency dependences of dielectric constant ϵ' , loss ϵ'' and conductivity κ' of Fe_3O_4 at 37 K.
 (b) Complex plane plots of (a).

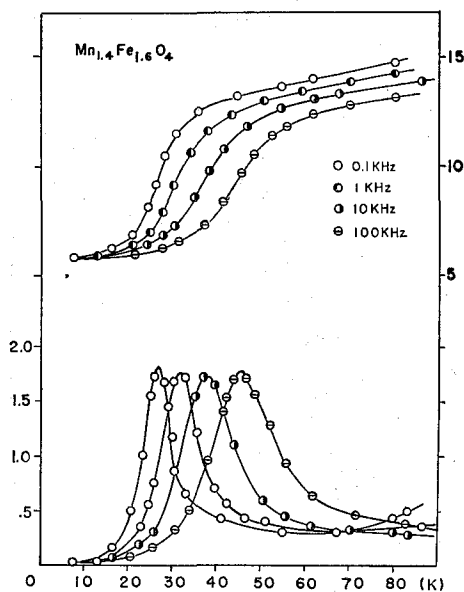


Fig. 5. Temperature dependences of dielectric constant and dielectric loss of $\text{Mn}_{1.4}\text{Fe}_{1.6}\text{O}_4$.

Containing a considerable amount of Fe^{2+} ions, $\text{Zn}_{0.6}\text{Fe}_{2.4}\text{O}_4$ showed such a large loss peak as Fe_3O_4 . Complex plane plots of the dispersion of $\text{Zn}_{0.6}\text{Fe}_{2.4}\text{O}_4$ are shown in Fig. 9. Figures 10 to 12 show the results of $\text{Mn}_{0.59}\text{Zn}_{0.33}\text{Fe}_{2.08}\text{O}_4$ precipitated from aqueous solution. This sample had not so much Fe^{2+} ions and was similar to $\text{Mn}_{1.4}\text{Fe}_{1.6}\text{O}_4$ in the dielectric dispersion. The results of $\text{Mn}_{0.8}\text{Fe}_{2.2}\text{O}_4$ are shown in Figs. 13 to 15. $\text{Mn}_{0.8}\text{Fe}_{2.2}\text{O}_4$ probably contained more Fe^{2+} ions than $\text{Mn}_{1.4}\text{Fe}_{1.6}\text{O}_4$ but it was difficult to know the precise amount of Fe^{2+} ions in the sample because some

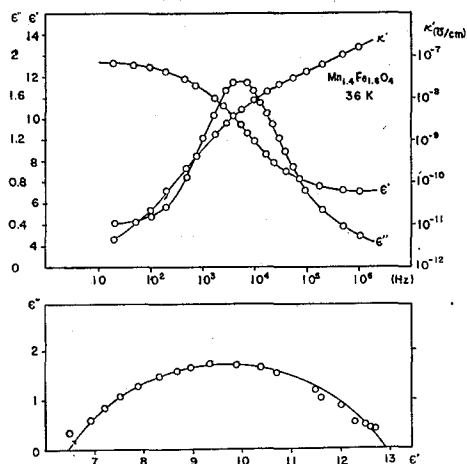


Fig. 6. Frequency dependences of dielectric constant ϵ' , loss ϵ'' and conductivity κ' of $\text{Mn}_{1.4}\text{Fe}_{1.6}\text{O}_4$ at 36 K.

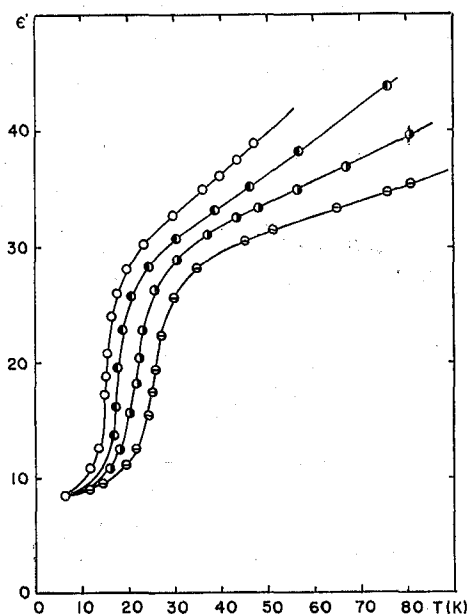


Fig. 7. Temperature dependence of dielectric constant ϵ' of $\text{Zn}_{0.6}\text{Fe}_{2.4}\text{O}_4$.

Mn ions became divalent. ZnFe_2O_4 containing no Fe^{2+} ions showed no dielectric relaxation. The observed results of dielectric dispersion are summarized in Table I. At about 30 K dielectric relaxations were found in all the ferrites containing ferrous ions, while no relaxation was found in ZnFe_2O_4 sample containing no ferrous ion.

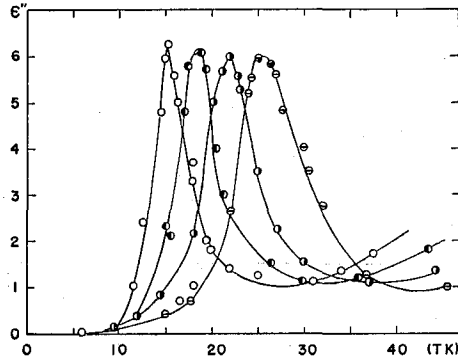


Fig. 8. Temperature dependence of dielectric loss ϵ'' of $\text{Zn}_{0.6}\text{Fe}_{2.4}\text{O}_4$.

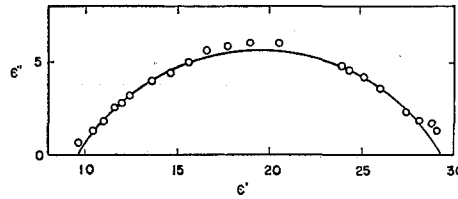


Fig. 9. Complex plane plots of dielectric constant ϵ' and loss ϵ'' of $\text{Zn}_{0.6}\text{Fe}_{2.4}\text{O}_4$ at 20 K.

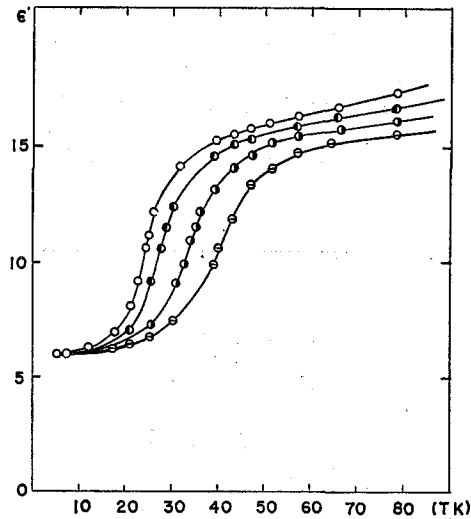


Fig. 10. Temperature dependence of dielectric constant ϵ' of $\text{Mn}_{0.59}\text{Zn}_{0.33}\text{Fe}_{2.08}\text{O}_4$.

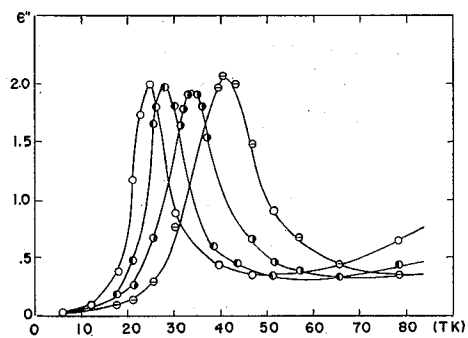


Fig. 11. Temperature dependence of dielectric loss ϵ'' of $\text{Mn}_{0.59}\text{Zn}_{0.33}\text{Fe}_{2.08}\text{O}_4$.

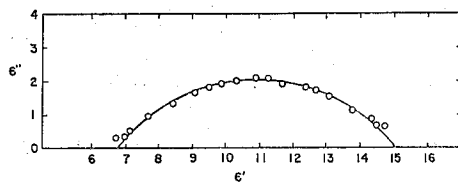


Fig. 12. Complex plane plots for $\text{Mn}_{0.59}\text{Zn}_{0.33}\text{Fe}_{2.08}\text{O}_4$ at 20.4 K.

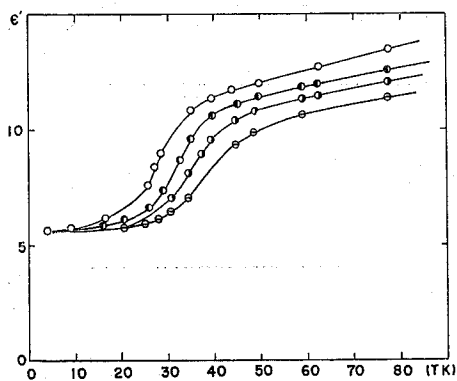


Fig. 13. Temperature dependence of dielectric constant ϵ' of $\text{Mn}_{0.8}\text{Fe}_{2.2}\text{O}_4$.

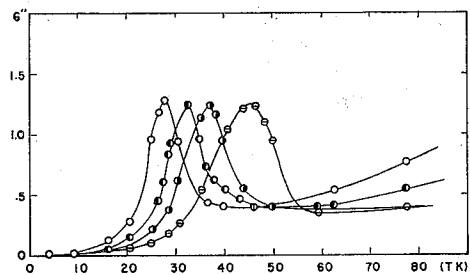


Fig. 14. Temperature dependence of dielectric loss ϵ'' of $\text{Mn}_{0.8}\text{Fe}_{2.2}\text{O}_4$.

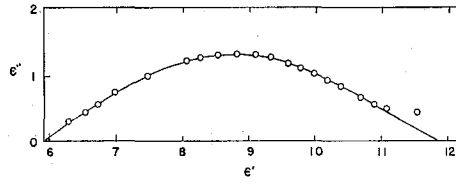
Fig. 15. Complex plane plots for $\text{Mn}_{0.8}\text{Fe}_{2.2}\text{O}_4$ at 35.2 K.

Table I. The Observed Results of Dielectric Dispersions

	ϵ_l	ϵ_h	$\Delta\epsilon$	ϵ_{4K}	$T(\text{K})$	$f_{\max}(\text{KHz})$
Fe_3O_4	62	9.2	52.8	7.4	37.0	2.0
$\text{Zn}_{0.6}\text{Fe}_{2.4}\text{O}_4$	29.4	9.5	19.9	8.2	20.0	3.5
$\text{Mn}_{1.4}\text{Fe}_{1.6}\text{O}_4$	12.9	6.43	6.47	5.8	36.0	5.5
$\text{Mn}_{0.8}\text{Fe}_{2.2}\text{O}_4$	11.6	5.99	5.61	5.7	35.2	4.0
$\text{Mn}_{0.59}\text{Zn}_{0.33}\text{Fe}_{2.08}\text{O}_4$	15.15	6.7	8.45	6.0	30.4	3.0
ZnFe_2O_4	6.06	6.06	0	6.06		

ϵ_l, ϵ_h : the limiting values of dielectric constant at lower and higher frequencies respectively

$\Delta\epsilon$: $\epsilon_l - \epsilon_h$

ϵ_{4K} : the value of dielectric constant ϵ at 4 K

$T(\text{K})$: the temperature at which the dielectric dispersion was observed

f_{\max} : the frequency at which dielectric loss becomes maximum at $T(\text{K})$

DISCUSSION

The values of dielectric constant ϵ' at 4.2 K were almost same (6~8). These dielectric constants are considered to come from electronic and ionic polarization. In Table I Fe_3O_4 and $\text{Zn}_{0.6}\text{Fe}_{2.4}\text{O}_4$ show higher relaxation intensity (the magnitude of dielectric dispersion) than $\text{Mn}_{1.4}\text{Fe}_{1.6}\text{O}_4$, $\text{Mn}_{0.8}\text{Fe}_{2.2}\text{O}_4$ and $\text{Mn}_{0.59}\text{Zn}_{0.33}\text{Fe}_{2.08}\text{O}_4$. No dielectric relaxation was observed in ZnFe_2O_4 . The stoichiometric Fe_3O_4 contains 33% Fe^{2+} ions but powder samples of Fe_3O_4 in this experiment contain ~31% Fe^{2+} ions because of the oxidation. It is impossible to make a chemical analysis of the ferrous ions in the ferrites containing Mn ions because Mn ions change the valence in the process of the analysis. Mössbauer measurements and NMR measurements give rough estimates of the ferrous contents but no precise ones. In order to compare ferrous contents in these ferrites relatively we compared the electrical conductivities of the ferrites. Since the hopping of electron between Fe^{2+} and Fe^{3+} ions play a main role in the electrical conduction of the ferrites, the electrical conductivity is considered to change in proportion to the ferrous content in the ferrites. Table II shows the comparison between relaxation intensity and electrical conductivity. Fe_3O_4 and $\text{Zn}_{0.6}\text{Fe}_{2.4}\text{O}_4$ have high conductivity compared with other ferrites and have high relaxation intensity. $\text{Mn}_{1.4}\text{Fe}_{1.6}\text{O}_4$, $\text{Mn}_{0.8}\text{Fe}_{2.2}\text{O}_4$, and $\text{Mn}_{0.59}\text{Zn}_{0.33}\text{Fe}_{2.08}\text{O}_4$ have low conductivities and low relaxation intensities. ZnFe_2O_4 with a very low electrical conductivity showed no dielectric relaxation. From this table it is clear that relaxation intensities are proportional to the concentration of ferrous ions in the ferrites. Therefore, it seems that ferrous ions give origin to the dielectric relaxation.

Table II. Comparison between Relaxation Intensity and Conductivity

	$\Delta\epsilon$	Conductivity (20°C)
Fe_3O_4	52.8	$4.39 \times 10^{-4} \Omega/\text{cm}$
$\text{Zn}_{0.6}\text{Fe}_{2.4}\text{O}_4$	19.9	1.61×10^{-4}
$\text{Mn}_{1.4}\text{Fe}_{1.6}\text{O}_4$	6.47	7.64×10^{-6}
$\text{Mn}_{0.8}\text{Fe}_{2.2}\text{O}_4$	5.61	1.8×10^{-5}
$\text{Mn}_{0.59}\text{Zn}_{0.33}\text{Fe}_{2.08}\text{O}_4$	8.45	2.94×10^{-6}
ZnFe_2O_4	0	1.89×10^{-10}

Table III. Comparison of Activation Energies Obtained from the Temperature Dependence of Electrical Conductivity and those Obtained from the Temperature Dependence of Relaxation Times in Dielectric Relaxation

	Activation Energy (eV) (Conductivity)	Activation Energy (eV) (Dielectric Relaxation)
Fe_3O_4	4.0×10^{-2}	5.72×10^{-2}
$\text{Zn}_{0.6}\text{Fe}_{2.4}\text{O}_4$	3.93×10^{-2}	3.21×10^{-2}
$\text{Mn}_{1.4}\text{Fe}_{1.6}\text{O}_4$	2.15×10^{-2}	4.45×10^{-2}
$\text{Mn}_{0.8}\text{Fe}_{2.2}\text{O}_4$	—	4.43×10^{-2}
$\text{Mn}_{0.59}\text{Zn}_{0.33}\text{Fe}_{2.08}\text{O}_4$	4.22×10^{-2}	4.0×10^{-2}
ZnFe_2O_4	—	—

Table III shows the comparison of the activation energies obtained from the temperature dependence of d.c. electrical conductivity near 30 K and those from the temperature dependence of relaxation times in dielectric relaxation. Both activation energies coincide fairly well with each other. All ferrite samples in this Table have the energy of $\sim 1 \times 10^{-2}$ eV which is small compared with the ionic or atomic process ($0.1 \sim 1$ eV)^{5,6}. This seems to correspond to the electronic process. The fact that activation energies obtained from the temperature dependence of electrical conductivity are in accordance with those from the temperature dependence of relaxation times means that both electrical conductivity and dielectric relaxation originated in the same mechanism. Therefore, this dielectric relaxation is considered to be caused by the hopping of electron between Fe^{2+} and Fe^{3+} ions.

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